



Reducing diffusion induced stress in planar electrodes by plastic shakedown and cyclic plasticity of current collector



Yicheng Song^{a,b,*}, Zongzan Li^c, Junqian Zhang^{a,b}

^a Department of Mechanics, Shanghai University, Shanghai 200444, China

^b Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai University, Shanghai 200072, China

^c Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, China

HIGHLIGHTS

- A strategy to reduce stress and enhance capacity by plastic yield of current collector.
- Identify 3 elastoplastic types: pure elastic, plastic shakedown, cyclic plasticity.
- Plastic shakedown reduces stress and enhances capacity with good safety.
- Cyclic plasticity further reduces stress and enhances capacity.
- Design schemes are provided for plastic shakedown and cyclic plasticity.

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ABSTRACT

This paper proposes a strategy to reduce the diffusion induced stress and enhance the capacity of a layered electrode by allowing the plastic deformation of current collector. Based on analytical formulations of the stress in whole electrode, three types of elastoplastic behaviors of current collector, i.e. pure elastic deformation, plastic shakedown and cyclic plasticity, are identified. Criteria separating the three cases are proposed. It is found applying a thin current collector and allowing it to plastically yield in the charge/discharge cycles is beneficial not only to capacity as more space can be provided for active materials but also to electrochemical stability because the stress in active layer is significantly reduced. Structural design corresponding to plastic shakedown shows good balance between the said improvements and structural safety, whereas the case of cyclic plasticity further enhances the improvements. Therefore, structural designing scheme is provided for the former case according to the criterion of plastic shakedown but for the latter one based on the Coffin–Manson relation with expected cycle life.

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1. Introduction

Lithium ion batteries have been widely used in the applications from portable electronics to electric vehicles. The electrode of lithium ion battery usually employs a multilayer structure which is composed of active materials such as graphite, silicon or LiCoO_2 , and current collector made of copper or aluminum. In the cycles of charge and discharge, stress field is developed in the whole electrode partially because the lithiation induced deformation of active layer is restricted by the current collector, leading to mechanical and further electrochemical degradation of the electrodes [1].

Among the intensive studies devoted to the diffusion induced stress (DIS), the current collector was customarily considered as an elastic material [2–5]. Mechanical plastic yield is usually avoided perhaps because of the traditional believe in mechanical design that plastic deformation is harmful to structural safety. However, the main function of current collector in batteries is to provide a passageway for electron transportation, not for load bearing. In addition, if the current collector plastically yields in charge and discharge, the relaxation brought by the plastic deformation may reduce the stress in active layer from which the electrochemical performance may benefit. Therefore, this article attempts to explore the possibility of allowing the plastic deformation of current collector in designing and taking advantage of the elastoplastic behavior of current collector to improve the performance of a battery. In literature, although the plastic yield of active material

* Corresponding author. Department of Mechanics, Shanghai University, Shanghai 200444, China.

E-mail addresses: yicheng_s@hotmail.com, ycsong@shu.edu.cn (Y. Song).

has been widely discussed [6–14], the impacts of plastic yield of current collector have been rarely investigated.

In this manuscript, we will demonstrate a strategy to reduce the DIS and enhance the capacity of a layered electrode by applying a thin current collector whose plastic deformation is utilized. There are three types of possible elastoplastic behaviors for the current collector, i.e. pure elastic deformation (PED), plastic shakedown (PS) and cyclic plasticity (CP). See Fig. 1, taking a cyclic uniaxial tension/compression test as example, pure elastic deformation is one in which plastic yield does not occur. Plastic shakedown is one in which plastic yield takes place only during the first loading, while the subsequent unloading and reloading are perfectly elastic. Cyclic plasticity is one in which alternating plastic yield of the material takes place in each loading–unloading cycle, leading to a closed elastic–plastic loop.

In order to characterize the impacts of the elastoplastic behavior of current collector on battery performance and designing insights, an analytical model will be established for a planar layered electrode. Yield criterion of current collector will be proposed, taking into account the impacts of material properties, electrode configuration and charging states. Evolutions of the stresses in both current collector and active layer in the cycles of charge and discharge will be simulated. Finally, designing insights will be provided based on the discussions.

2. Methodology

Consider a layered electrode in which two active layers of equal thickness h_1 are symmetrically bonded to a current collector of thickness h_c , Fig. 2. Let the thickness direction be aligned with the z -axis and the in-plane of plate with x - and y -axes. Lithium ions are inserted into and extracted out of the electrode from both side surfaces.

The Li-ion diffusion in the active layer is assumed to be governed by Fick's law. Other factors affecting the diffusion such as saturation cap [15], stress coupling [16], and concentration dependent elastic modulus [2,17], are neglected because the focus here is to investigate the impacts of plastic yield of current collector. Therefore, the diffusion is described by

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad (1)$$

where c is the molar concentration of Li-ions in the plate, D is the diffusivity of lithium ions.

Consider a full cycle, see Fig. 3. Both charge and discharge start with galvanostatic operation followed by potentiostatic operation.

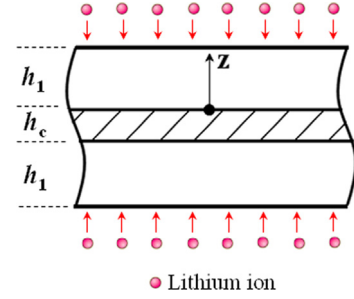


Fig. 2. The symmetric layered electrode investigated in this work.

In the charge phase of the cycle the lithiation of anode starts from a lithium free state. Hence, the initial condition and the boundary conditions for galvanostatic charging are

$$c = 0 \quad \text{for } t = 0 \quad (2a)$$

$$D \frac{\partial c}{\partial z} = \frac{i_n}{F} \quad \text{for } z = h_1 \quad (2b)$$

$$D \frac{\partial c}{\partial z} = 0 \quad \text{for } z = 0 \quad (2c)$$

where $F = 96485.3 \text{ C mol}^{-1}$ is Faraday's constant and i_n is the surface current density which is positive for lithiation but negative for delithiation. Due to the symmetry, only the equations of the upper active layer are provided. The distribution of Li-ion concentration is provided by Crank [18]:

$$c(z, t) = \frac{i_n h_1}{FD} \left\{ \frac{Dt}{h_1^2} + \frac{3z^2 - h_1^2}{6h_1^2} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cos \frac{n\pi z}{h_1} \exp \left(-n^2 \pi^2 \frac{Dt}{h_1^2} \right) \right\} \quad (3)$$

It is assumed that the charge operation switches from the galvanostatic to the potentiostatic at the time moment t_0 with Li-ion concentration $c(z, t_0)$. Hence, the initial and boundary conditions for potentiostatic charging are

$$c = c(z, t_0) \quad \text{for } t = t_0 \quad (4a)$$

$$c = c_0 \quad \text{for } z = h_1 \quad (4b)$$

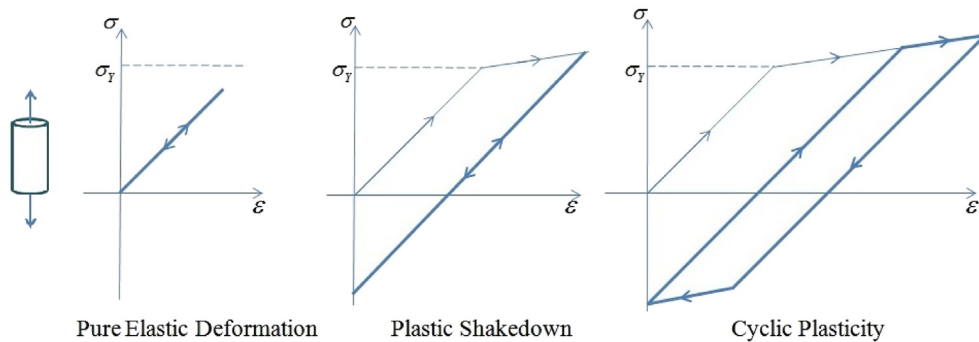


Fig. 1. Explanation of the terms "pure elastic deformation", "plastic shakedown" and "cyclic plasticity" with the stress–strain curve of a strain controlled uniaxial tension/compression test. σ_y is the yield strength.

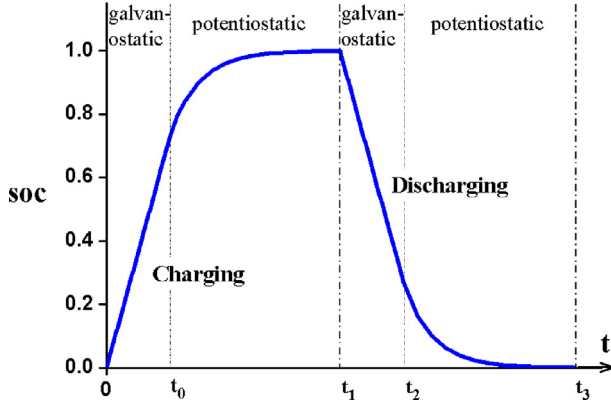


Fig. 3. Illustration of one cycle of charge and discharge.

$$D \frac{\partial c}{\partial z} = 0 \quad \text{for } z = 0 \quad (4c)$$

where c_0 is the constant concentration at the charging surface. The expression for $c(z, t_0)$ is obtained by Equation (3) with insertion $t = t_0$. The solution can be obtained by using the method of separation of variables and is written as

$$c(z, t) = c_0 - \sum_{n=1}^{\infty} \left\{ \frac{2}{h_1} \int_0^{h_1} [c_0 - c(z, t_0)] \cos \left[\frac{(2n-1)\pi}{2h_1} z \right] dz \cdot \exp \left[\frac{(2n-1)^2 \pi^2 D (t - t_0)}{4h_1^2} \right] \cdot \cos \left[\frac{(2n-1)\pi}{2h_1} z \right] \right\} \quad (5)$$

In the discharging phase of the full cycle the delithiation will start with galvanostatic operation from the saturation state having homogenous lithium-ion distribution, and continue with potentiostatic operation from the time moment $t = t_2$. The delithiated Li-ions of galvanostatic discharging can be obtained by simply using Equation (3) with the replacement of t by discharging time $(t - t_1)$. And the delithiated Li-ions during the follow-up potentiostatic discharging can be obtained by Equation (5) with replacement of t and t_0 by discharging time $(t - t_1)$ and $(t_2 - t_1)$.

Considering that the layered electrode is large and the Li-ions are inserted symmetrically, the electrode does not bend. Among the totally six stress components, only the two in-plane biaxial stresses σ_x and σ_y are non-zero. The out-of-plane stress σ_z , which arises from the compression by adjacent electrodes, is neglected as it is small and considered incapable of significantly impacting the elastoplastic behavior of current collector. Because $\sigma_x = \sigma_y$, we use σ_1 and σ_c to denote the biaxial stress in the active layer and current collector, respectively. According to the equilibrium condition, σ_1 and σ_c must satisfy

$$2 \int_0^{h_1} \sigma_1 dz + \int_{-h_c}^0 \sigma_c dz = 0 \quad (6)$$

Focusing on the active materials like graphite and LiFePO_4 which do not show significant plastic behaviors, the active material layers are assumed to be isotropic and always elastic. In the active layer the stress σ_1 is

$$\sigma_1 = E'(\epsilon_0 - \Omega c/3) \quad (7)$$

where ϵ_0 is the in-plane strain of the plate electrode, Ω is the partial molar volume, $E' = E/(1 - \nu)$ is the biaxial modulus and ν is the Poisson's ratio.

The current collector is considered as an elastoplastic material with linear kinematic hardening behavior, see Fig. 4. Its elastic modulus is E_c , plastic modulus E_p , and yield strength σ_y . In charge process the current collector is stretched due to the expansion of active materials, while in discharging the current collector is unloaded due to the shrinkage of active materials.

When the current collector is elastic, the biaxial stress σ_c develops linearly with the in-plane strain ϵ_0 . In the linear hardening stage after the current collector yields, the equivalent stress $\sigma_e = \sqrt{3s_{ij}s_{ij}/2}$ changes linearly with the equivalent plastic strain $\bar{\epsilon}^p = \sqrt{2\epsilon_{ij}^p\epsilon_{ij}^p/3}$. In the elastic unloading stage, the incremental stress $\Delta\sigma_c$ is linear to the incremental strain $\Delta\epsilon_0$. In the reversing hardening stage the incremental equivalent stress is proportional to the incremental equivalent plastic strain. The cyclic plastic constitutive behavior is depicted in Fig. 4 and described as

$$\sigma_c = E'_c \epsilon_0 \quad \text{for } \bar{\epsilon}^p = 0 \quad (8a)$$

$$\Delta\sigma_e = E_p \Delta\bar{\epsilon}^p \quad \text{for } \bar{\epsilon}^p \neq 0, d\bar{\epsilon}^p > 0 \quad (8b)$$

$$\Delta\sigma_c = E'_c \Delta\epsilon_0 \quad \text{for } \bar{\epsilon}^p \neq 0, d\bar{\epsilon}^p = 0 \quad (8c)$$

where $E'_c = E_c/(1 - \nu)$ is the biaxial modulus of the current collector. Note that $s_{ij} = \sigma_{ij} - \sigma_{kk}\delta_{ij}/3$ is the deviatoric stress, and the plastic strain $\epsilon_x^p = -2\epsilon_y^p = -2\epsilon_z^p$ due to the assumption of plastic incompressibility, we have

$$\sigma_e = \sigma_c \quad (9a)$$

$$\bar{\epsilon}^p = 2\epsilon_x^p = 2\epsilon_y^p \quad (9b)$$

Substitute Equations (7) and (8a) into Equation (6), the biaxial stresses in the current collector and active layer in elastic stage are

$$\sigma_c = \frac{1}{3} \frac{E'_c \Omega c_s}{\Gamma_1} Q \quad (10a)$$

$$\sigma_1 = \frac{1}{3} \frac{E' \Omega c_s}{\Gamma_1} Q - \frac{1}{3} E' \Omega c \quad (10b)$$

where $\Gamma_1 = 1 + 1/2E_c/E_1h_c/h_1$ is a dimensionless variable determined by the modulus ratio and thickness ratio, $Q = 1/c_s h_1 \int_0^{h_1} c dz$ is the SOC (state of charge) and c_s is the saturation concentration at stoichiometric limit.

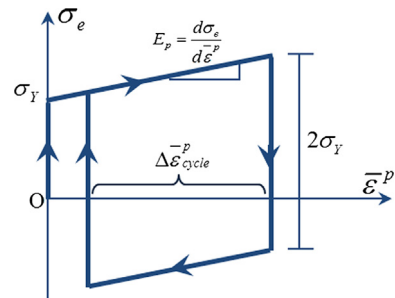


Fig. 4. Illustration of the plastic constitutive behavior of the current collector. $\Delta\bar{\epsilon}^p_{\text{cycle}}$ is the plastic strain range.

In the plastic hardening stage of charge

$$\sigma_c = \frac{\sigma_Y}{\Gamma_2} + \frac{2E_p\Omega c_s}{3\Gamma_2}Q \quad (11a)$$

$$\sigma_1 = -\frac{1}{3}E'_1\Omega c - \frac{h_c}{h_1}\frac{\sigma_Y}{2\Gamma_2} + \left(1 + \frac{2E_p}{E'_c}\right)\frac{E'_1\Omega c_s}{3\Gamma_2}Q \quad (11b)$$

where $\Gamma_2 = h_c/h_1 E_p/E'_1 + 1 + 2E_p/E'_c$. In the elastic unloading stage, taking the end of charging as the reference state, the incremental stresses are

$$\Delta\sigma_c = \frac{E'_c\Omega c_s}{3\Gamma_1}\Delta Q \quad (12a)$$

$$\Delta\sigma_1 = \frac{E'_1\Omega c_s}{3\Gamma_1}\Delta Q - \frac{1}{3}E'_1\Omega\Delta c \quad (12b)$$

In this stage, reversing yield would be induced if $\Delta\sigma_c$ exceeds $2\sigma_Y$. Whereas if $\Delta\sigma_c$ is smaller than $2\sigma_Y$, there would be no reversing yield and the current collector is unloaded and reloaded elastically in the following cycles.

In the reversing hardening stage after the reversing yield, the incremental equivalent stress $\Delta\sigma_e$ is again linear to the incremental equivalent plastic strain $\Delta\bar{\epsilon}^p$. Similar to Equations (11a) and (11b), we have

$$\Delta\sigma_c = \frac{2E_p\Omega c_s}{3\Gamma_2}\Delta Q \quad (13a)$$

$$\Delta\sigma_1 = \left(1 + \frac{2E_p}{E'_c}\right)\frac{E'_1\Omega c_s}{3\Gamma_2}\Delta Q - \frac{1}{3}E'_1\Omega\Delta c \quad (13b)$$

Finally in the elastic reloading stage, the stresses develop again linearly with the in-plane strain as described by Equations (12a) and (12b).

In the cycles, the plastic strain range $\Delta\bar{\epsilon}_{\text{cycle}}^p$ is very important as it directly impacts the low-cycle fatigue life (Here $\Delta\bar{\epsilon}_{\text{cycle}}^p$ is used to distinguish from the incremental plastic strain $\Delta\bar{\epsilon}^p$). According to Fig. 4, the plastic strain range $\Delta\bar{\epsilon}_{\text{cycle}}^p$ is equal to the incremental plastic strain in the reversing hardening stage. Therefore, according to Equations (13a) and (8b)

$$\Delta\bar{\epsilon}_{\text{cycle}}^p = \frac{2\Omega c_s}{3\Gamma_2}(Q_s - 2Q_Y) \quad (14)$$

where Q_s is the saturation SOC when delithiation starts, Q_Y is the SOC corresponding to the initial yield and can be determined by Equation (10a), thus $Q_s - 2Q_Y$ corresponds to the change of SOC in reversing hardening stage.

3. Results and discussions

3.1. Yield criterion, plastic shakedown and cyclic plasticity

Firstly we discuss the yield criterion. The current collector yields when the equivalent stress reaches yield strength, i.e. $\sigma_e = \sigma_Y$. Introducing Equations (9a) and (10a), we have the yield criterion

$$\frac{1}{\frac{E'_1}{E'_c} + \frac{1}{2}\frac{h_c}{h_1}}Q = \bar{\sigma}_Y \quad (15)$$

where $\bar{\sigma}_Y = 3\sigma_Y/E'_1\Omega c_s$ is the dimensionless yield stress. This criterion, depicted in Fig. 5 using the red line (in the web version), indicates that active materials with lower elastic modulus E_1 and

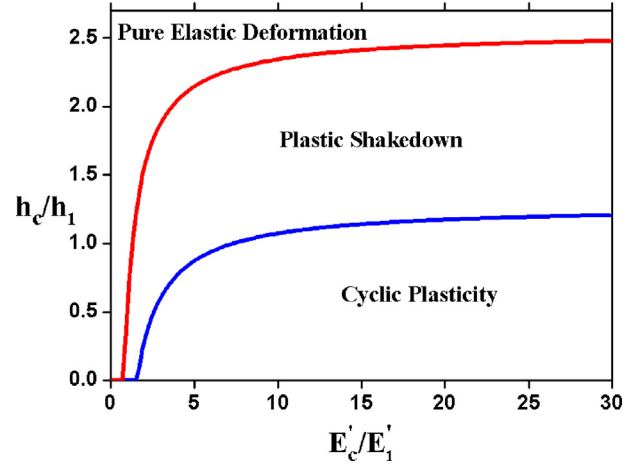


Fig. 5. Yield map showing the separation of three types of elastoplastic behaviors of current collector, i.e. pure elastic deformation, plastic shakedown and cyclic plasticity, with respect to the elastic modulus ratio E'_c/E'_1 and thickness ratio h_c/h_1 . This map is for fully charged graphite electrodes.

smaller lithiation induced strain Ωc_s are favored to avoid the plastic yield of current collector. In addition, the elastic modulus ratio and thickness ratio of current collector to active material also impact the yield.

Once yields, the current collector may exhibit two types of plastic behaviors in the following cycles, i.e. plastic shakedown and cyclic plasticity. In the former case the unloading and reloading is purely elastic, see Fig. 1(b). While in the latter case alternating plastic yield takes place in each loading–unloading cycle, see Fig. 1(c). Consider a discharge operation from saturation state to lithium-free state in which $\Delta Q = Q_s$, reversing yield takes place once the incremental stress $\Delta\sigma_c$ exceeds $2\sigma_Y$. Introducing this condition into Equation (12a), the critical condition distinguishing between plastic shakedown and cyclic plasticity is obtained as

$$\frac{1}{\frac{E'_1}{E'_c} + \frac{1}{2}\frac{h_c}{h_1}}\frac{Q_s}{2} = \bar{\sigma}_Y \quad (16)$$

This critical condition is plotted in Fig. 5 using the blue line. Comparing Equations (16) with Equation (15) and noting Q_Y is the SOC corresponding to the first yield, it is clear that plastic shakedown takes place if the initial yield of current collector occurs after the electrode has been charged half full, i.e. $Q_Y \geq 0.5Q_s$, whereas cyclic plasticity will be induced when $Q_Y < 0.5Q_s$.

A yield map is provided based on the above critical conditions, see Fig. 5. This figure shows separation of the three possible elastoplastic behaviors of current collector in a fully charged graphite electrode. It shows that the elastoplastic type changes from pure elastic deformation to plastic shakedown and further to cyclic plasticity with increasing elastic modulus ratio E'_c/E'_1 as well as decreasing thickness ratio h_c/h_1 . The reason is that the current collector with higher E'_c applies stronger restriction to the active layer, and smaller thickness h_c results in smaller cross-sectional area of the current collector, both of which lead to higher stress and larger plastic strain in the current collector during the cycles.

According to Fig. 5, the thickness ratio h_c/h_1 is preferably higher than 2.4 to avoid the plastic yield of current collector if we choose a copper–graphite electrode whose modulus ratio E'_c/E'_1 is about 10. This thickness ratio is higher than that employed in real electrodes [19]. It may be an error induced by assigning the maximum lithiation induced volumetric strain $\Omega c_s = 8\%$ of pure graphite to the

graphite composite whose Ω_c should be smaller due to the existence of pores and other non-active compositions in the composite. Therefore, the structural designs provided by this paper are considered conservative.

3.2. Diffusion induced stresses

In the following sections, impacts of the plastic yield of current collector on DISEs will be discussed. The current collector is chosen as copper and the active material as graphite. The employed material constants of copper are yield strength $\sigma_Y = 300$ MPa, elastic modulus $E_c = 150$ GPa and plastic modulus $E_p = 3$ GPa. The elastic modulus of graphite is $E_1 = 15$ GPa. The operation of charge and discharge follows that provided by Fig. 3.

Fig. 6(a) and (b) shows the stresses along plate thickness in a time moment after the current collector has yielded in charge and discharge, respectively. The thickness ratio h_c/h_1 is set to 0.25 according to Fig. 5 to ensure the plastic yield of current collector. It is found that the estimations of stresses, in both current collector and active layer, are significantly higher once the plastic yield of current collector is neglected. The reason is that a substantial amount of diffusion induced stress in the layered electrode arises from the constraint of active layer by current collector. Once the current collector yields, the plastic relaxation enables the layered electrode occur relatively large deformation with respect to small increment of stress. Therefore, ignoring the plastic yield of current collector

may lead to overestimations of the stresses and underestimations of the strength of electrodes.

As seen, the diffusion induced stresses in active layers can be reduced by the plastic relaxation of current collector. Therefore, Fig. 7 is further prepared to illustrate the impacts of the plastic yield by plotting the evolutions of the DISEs in certain positions of the electrode in cycles. According to the yield map provided by Fig. 5,

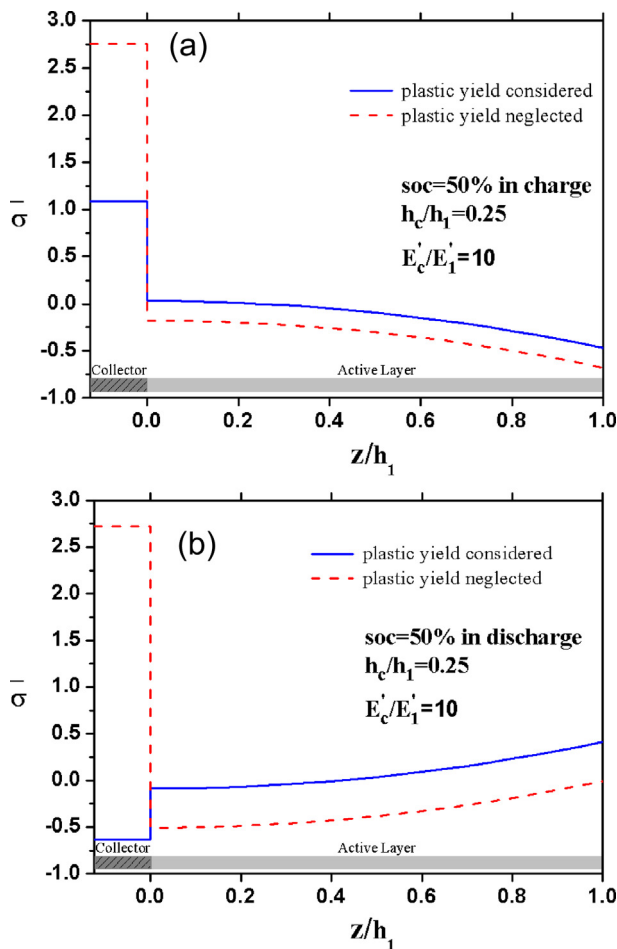


Fig. 6. The dimensionless biaxial stress $\bar{\sigma} = 3\sigma/E'_1\Omega_c$ in the electrode: (a) in charge process, and (b) in discharge process.

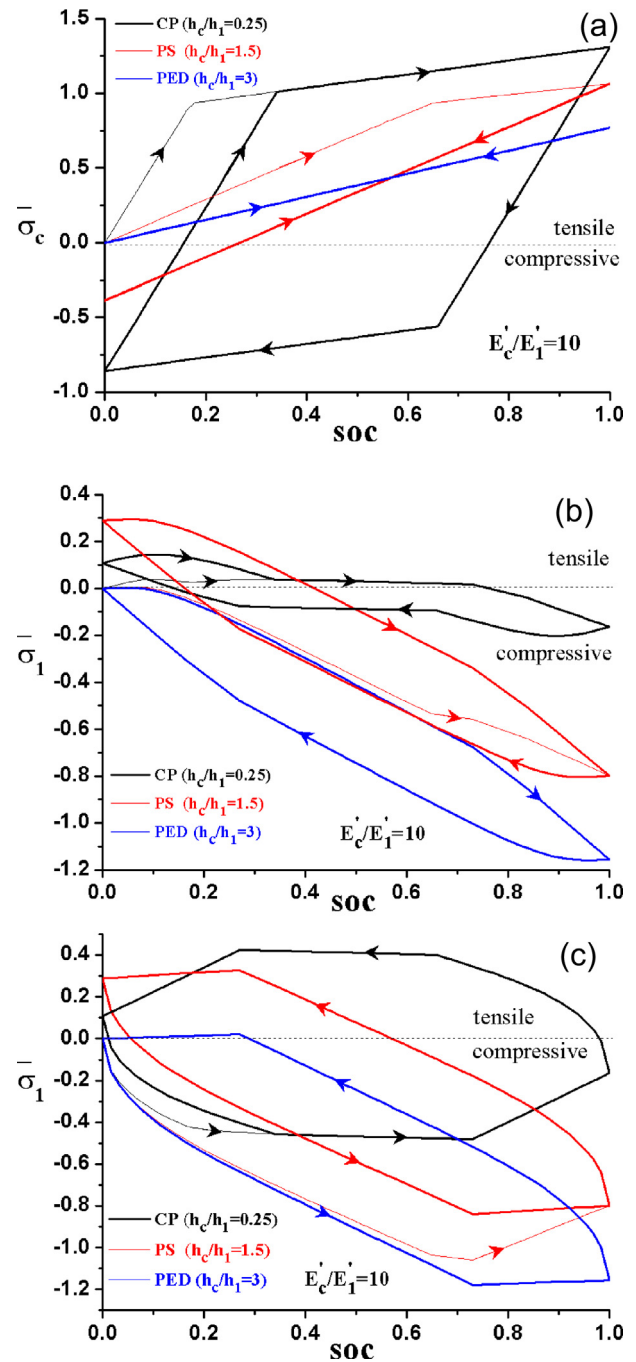


Fig. 7. Evolutions of the biaxial stress against SOC in cycles of charge and discharge: (a) in the current collector, (b) at the interface between current collector and active layer where $z/h_1 = 0$, and (c) at the inlet surface where $z/h_1 = 1$. Three thickness ratios are employed according to Fig. 4 so that the blue, red and dark lines describe the cases of pure elastic deformation (PED), plastic shakedown (PS) and cyclic plasticity (CP), respectively. The thin lines represent the stresses in the first cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the thickness ratio h_c/h_1 is set to 3, 1.5 and 0.25, respectively, corresponding to the case of pure elastic deformation, plastic shakedown and cyclic plasticity.

Fig. 7(a) shows the evolutions of the stress in the current collector. It is clearly seen the change from pure elastic deformation to plastic shakedown and finally to cyclic plasticity with respect to decreasing thickness ratio. In the case of $h_c/h_1 = 3$, the current collector is thick so that it cannot be stretched to yield, the stress in current collector changes linearly with SOC. In the case of shakedown when $h_c/h_1 = 1.5$, the plastic strain is limited and the stress in current collector changes linearly with SOC since the second cycle. Nonlinear behavior occurs only in the first charge. In the case of cyclic plasticity when $h_c/h_1 = 0.25$, the current collector is too thin so that the current collector yields in every charge and discharge and the stress evolves in the form of a closed loop. With the change of plastic type, the stress in current collector evolves in larger ranges with higher peak values and higher residual stresses.

Fig. 7(b) and (c) illustrates the stresses in the position of $z/h_1 = 0$ and $z/h_1 = 1$ in the active layer, respectively. It is seen that both the peak compressive stress and cyclic stress range in the charge/discharge cycle are significantly decreased when the elastoplastic type changes from pure elastic deformation to cyclic plasticity, although tensile stress is increased due to the residual deformation of current collector. This figure for one hand reveals one mechanism how tensile stress is generated in anode, for the other hand it is interesting to see that applying thinner current collectors and allowing them to yield is beneficial to the integrity of active layer as the peak stress and the cyclic stress range are significantly decreased.

The designs allowing plastic yield show two advantages compared with that free of plastic yield. Firstly, the thickness of current collector is decreased significantly, with which electrode capacity can be enhanced as more space can be provided for the active materials. It is found in Fig. 7 that the thickness of current collector in the case of plastic shakedown is only about 50% of that in the case of pure elastic deformation. This ratio is even lower in the case of cyclic plasticity. Secondly, the cycle life of electrode may benefit from the plastic yield because both the peak stress and the cyclic stress range in active layers, which is critical to the mechanical fade and electrochemical stability, are significantly decreased. Therefore, applying a thinner current collector and allowing it to yield is beneficial not only to the capacity but also to the structural integrity and cycle life of electrode.

It should be noted that the stress in active layer is decreased with the sacrifice of higher stress and cyclic stress range in the thin current collector. However, this increase of stress may be not so important to the battery performance because current collector, which functions as a passageway of electrons, does not involve in the electrochemical reaction and storage of Li-ions. Therefore, this increase of stress in current collector may be acceptable on the condition that the plastic deformation does not lead to crack.

3.3. On the plastic yield

In this section we discuss whether the plastic yield of current collector is allowable. If yes, which type is better between plastic shakedown or cyclic plasticity? How to determine the thickness of current collector in designing?

For the first question, it is known plastic yield should be avoided for ordinary load-bearing structures because cyclic fatigue may lead to structural failure. However, the electrode of a Li-ion battery may be not so sensitive to fatigue for two reasons. Firstly, the cycle life of a real battery may be less than one thousand of times and one cycle of charge and discharge may take several hours to several days. They are considered not adequate to induce fracture in the case of

finite plastic strain because experiments showed that polycrystalline copper took more than 10^5 cycles to fracture with constant and low plastic strain amplitude [20]. Secondly, the materials of current collector like copper and aluminum are known with good ductility. The reported ultimate fracture strain of copper film is 6% [21], whereas the extreme in-plane strain ϵ_0 of the copper-graphite electrode is calculated as about 2.6%, which is limited by the expansion of graphite and far below the reported value. Therefore, finite plastic deformation of current collector may be allowable.

The second question is which type is better between plastic shakedown and cyclic plasticity. Generally, the case of plastic shakedown shows good balance among all aspects, e.g. capacity enhancing due to thinner current collector, better electrochemical stability due to lower stress in active layer, and good fatigue resistance due to the zero plastic strain range since the second cycle. Electrode structure can be designed according to the critical criterion of plastic shakedown provided by Equation (16). According to calculation, changing the thickness ratio h_c/h_1 from 2.4 to 1.1, corresponding to the transition from pure elastic deformation to plastic shakedown, may lead to a reduction of the volume of current collector by more than 50% as well as the decrease of stress in active layer by 40%.

Compared with plastic shakedown, the case of cyclic plasticity is even superior in the aspects of capacity enhancing and electrochemical stability, though the plastic yield in every reversal may lead to low-cycle fatigue and significant shortening of cycle life. The number of cycle to failure in low-cycle fatigue is usually characterized by the Coffin–Manson relation [22,23]:

$$\Delta \bar{\epsilon}_{\text{cycle}}^p = \epsilon_f' (N)^c \quad (17)$$

where N is the expected cycle number to failure, ϵ_f' is the fatigue ductility coefficient and c is the fatigue ductility exponent. Being aware that both ϵ_f' and c are known empirical constants for a given material, the allowed plastic strain range $\Delta \bar{\epsilon}_{\text{cycle}}^p$ thus can be determined according to the designed cycle numbers N . Finally, the thickness ratio h_c/h_1 can be looked up from Fig. 8. This designing method enhances electrode capacity and decreases the stress in active layer as much as possible with the aim of an expected cycle life.

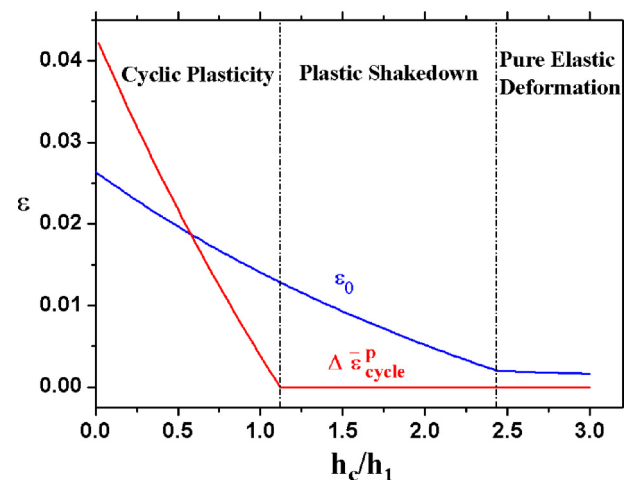


Fig. 8. The in-plane strain ϵ_0 of graphite-copper electrode and the plastic strain range $\Delta \bar{\epsilon}_{\text{cycle}}^p$ at saturation state vs. thickness ratio h_c/h_1 . The peak value of in-plane strain is about 2.6% when $h_c = 0$, consistent with the lithiation induced volumetric strain 8% of free expansion graphite.

4. Conclusions

This work studies the impacts of plastic yield of current collector on the diffusion induced stress in a symmetric layered electrode. Based on analytical formulations, three types of elastoplastic behaviors of current collector, i.e. pure elastic deformation, plastic shakedown and cyclic plasticity, are identified. Criteria separating the three cases are proposed. It is found the plastic behavior of current collector would change from pure elasticity to plastic shakedown and finally to cyclic plasticity with increasing elastic modulus ratio E_c/E_1 and decreasing thickness ratio h_c/h_1 of current collector to active layer.

As for the diffusion induced stress, it is found that neglecting the plastic yield of current collector would result in overestimations of the stress in whole electrode and underestimation of electrode strength. By simulating the evolution of stress in cycles of charge and discharge, it is suggested that applying a thin current collector and allowing finite plastic deformation is beneficial not only to the battery capacity as more space can be provided for active materials, but also to the electrochemical stability and cycle life of electrode because the stress in active layer is significantly decreased.

Regarding the plasticity of current collector, firstly finite plastic deformation is considered acceptable due to the few cycle numbers, long cycle period and limited plastic strain of current collector. Secondly, electrode structures responsible for plastic shakedown and cyclic plasticity are discussed and compared. The case of plastic shakedown shows good balance among all aspects, e.g. capacity enhancing due to thinner current collector, better electrochemical stability due to lower stress in active layer, and good fatigue resistance due to the zero plastic strain range. In contrast, the case of cyclic plasticity is even superior in the former two aspects but with the sacrifice that the cycle life is significantly shortened due to low-cycle fatigue. Therefore, structural design is provided by the critical criterion of plastic shakedown in the former case while by the Coffin–Manson relation according to an expected cycle life in the latter case.

It should be noted this paper discusses the impact of plastic yield by taking a graphite–copper anode for example. However, the main conclusion of this work, i.e. applying a thin current collector and allowing it to yield is beneficial to both the capacity and cycle life, is also applicable for cathode. The only difference is the sign of stress. For a cathode which is initially lithium-saturated and deformation free, the current collector would be compressed to yield in charge (delithiation) operation. In addition, applying a thin

current collector in cathode and allowing it to yield results in decrease of tensile stress in active layer.

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